Aqueous phase epoxidation of 1-butene catalyzed by suspension of Au/TiO_2 +TS-1

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Abstract

A combination of two catalysts, Au/TiO_2 and TS-1 were used to catalyze the demanding reaction of butene epoxidation in an aqueous solution using molecular oxygen under very mild reaction conditions. Peroxy initiator was not necessary but carbon monoxide as a sacrificial reductant was needed. Carbon monoxide conversions increase with time on stream suggesting the generation of a highly active aqueous phase CO oxidation catalyst.

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Introduction

Since the discovery by the group of Haruta [1] that supported Au catalysts have exceptional CO oxidation activities, these catalysts have been investigated extensively for many interesting gas phase reactions. Reviews on CO oxidation [2], WGS [3], hydrochlorination and hydrogenation [4] have been published. Recently, interesting oxidation reactions catalyzed by supported Au catalysts in the liquid phase have also attracted significant attention. Noteworthy examples include the selective oxidation of alkene [5], alcohol and glucose [6], and the formation of hydrogen peroxide from H_2 and O_2 [7]. In this article we examine two low temperature aqueous phase oxidation reactions, CO oxidation and alkene epoxidation, using a binary catalytic system of a physical mixture of Au/TiO_2 and TS-1.

There has been limited success in the epoxidation of unactivated alkenes with molecular oxygen because it is such a demanding reaction. The only known commercial processes are the Ag catalyzed epoxidation of ethylene [8] and butadiene [9]. These catalytic processes however fail when the alkene possesses allylic hydrogen. Recently, there has been extensive exploration using supported Au catalyst for alkene epoxidation with molecular O_2. These studies fall into three classes, those with molecular O_2 alone, those with the addition of a peroxy initiator, and those that require a sacrificial reductant. Very low turnovers of propene epoxidation were observed using H_2O, O_2, C_3H_6 over Au/TiO_2 catalysts [10]. Turner et. al. [11] reported oxidation of styrene to benzaldehyde, styrene epoxide and acetopheneone over Au_{55} clusters. However, the activity and the selectivity to epoxide were low. The addition of a peroxy initiator accelerated epoxidation reactions [5], but the product distribution appeared to be very solvent dependent. The most intensely studied system is one when H_2 was included as a sacrificial reductant, and the catalysts used were Au/TiO_2 [12], Au/TS-1 and Au/MCM-41 [13] and Au-Ba/Ti-TUD

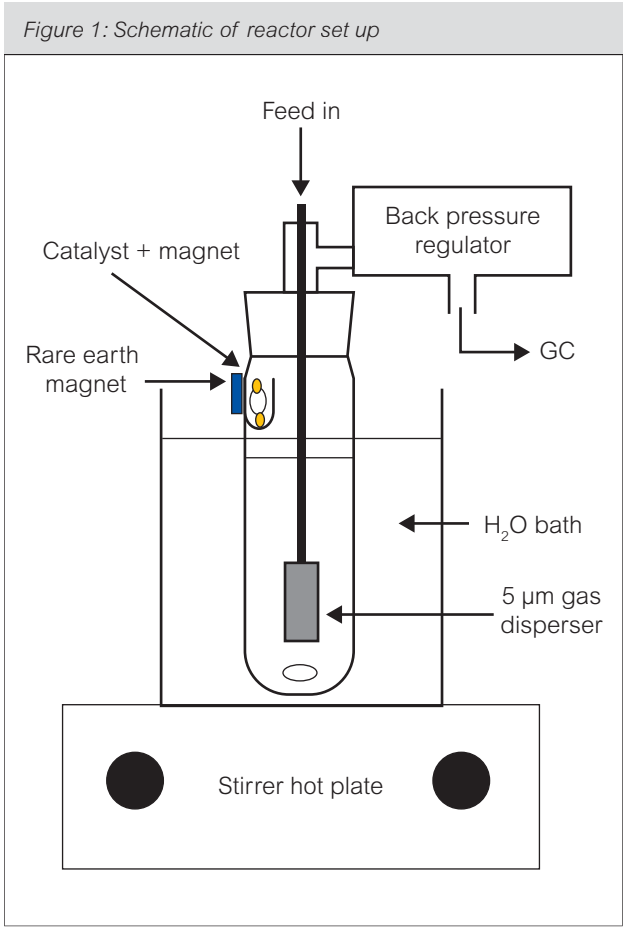
[14]. The proposed mechanism for these catalysts involves the formation of H_2O_2 on the Au active site and the migration of the peroxide onto neighboring Ti to form Ti hydroperoxy species which can donate an [O] atom to propylene to form propylene epoxide [14].

The epoxidation of C_3H_6 in the presence of H_2 and O_2 was conducted in the gas phase at moderately high temperature. Interestingly, the group of Robert J. Davis [15] reported in 2007 that Au/TiO_2 and Au/C were able to catalyze the formation of H_2O_2 in the aqueous phase at ambient temperature, using CO as a sacrificial reductant (Eq. 1)

$$CO+O_2+H_2O \rightarrow CO_2+H_2O_2 \quad (1)$$

This low temperature method to generate H_2O_2 may be safer than by H_2 oxidation at higher temperatures, and capturing this H_2O_2 for alkene epoxidation appears to be a very fruitful area of investigation. TS-1 is known to be an excellent catalyst for alkene epoxidation using H_2O_2 as the oxidant [16].

Figure 1: Schematic of reactor set up



A combination of Au/TiO_2 and TS-1 was then chosen for CO assisted butene epoxidation study. The effect of butene and TS-1 on CO oxidation was also investigated during the epoxidation reaction.

Methods

The two different batches of Au/TiO2 catalysts used in the reaction (no observable difference in the catalytic performance) were supplied by World Gold Council. The Au loadings of Au/TiO_2-02-4 and $Au-TiO_2$-02-9 were 1.51 and 1.49 wt. % and the average Au particle sizes were 3.8 ±1.5nm and 3.6±1.32 nm, respectively. TS-1 was synthesized using the method of Thangaraj et al. [17]. Diffuse reflectance UV visible spectroscopy (Perkin Elmer LAMBDA 1050) was used to verify the absence of extra framework Ti. The silicalite sample was synthesized using the same procedure as for TS-1, except that TiBuOH was omitted.

The epoxidation reaction was carried out in a high pressure glass reactor (Cole-Palmer) which contained 50 mL of ion-exchanged distilled water (DDI H_2O, pH~5.5). The reactor was maintained at 40°C (except when specified). The gas feed composition, 2.5% CO, 1.25% O_2 and 1.25% 1-butene, balance He, was adjusted using 5850E Brooks flow controllers. 40 mL min^{-1} of the feed gas was directed into the aqueous phase through a 5 µm stainless steel porous frit (Scientific Instrument Services). The pressure in the vessel was maintained at 480 kPa with a back pressure regulator (Mighty Mite). The experiments were started usually with the catalysts (0.1g Au/TiO_2 ±0.15 g TS-1) placed above the water level in a small polyethylene cup with a small magnet in the cup and held in place by a rare earth magnet placed outside the reactor (Fig1). At a predetermined time (defined as time=0), the rare earth magnetic, external to the reactor, was used to guide the cup of catalyst inside the reactor into the water, thereby initiating the aqueous phase catalytic reaction. After the reaction, 50 mL of H_2O was used to replace the H_2O-catalysts mixture and the feed was again introduced at 480 kPa to calibrate the GC peak areas so as to quantify the gas composition accurately. The exit gas from the reactor was monitored with GC. All liquid products were separated from the solid catalysts by filtration through a 0.2 µm PVDF membrane (Pall) and analyzed with an Agilent 6890 GC. The GC columns were Alltech carbosphere packed column for CO, O_2 and CO_2 and Alltech EC-wax capillary column (0.32 mm*30 m) for organics.

H_2O_2 was titrated by ceric sulfate using a Ferroin indicator. The indicator solution was prepared by dissolving 0.123 g iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) into 15 mL DDI water, then adding 0.259 g 1,10-phenanthroline. The titration solution, 0.6875 mM $Ce(SO_4)_2$, was prepared by dissolving 0.114 g cerium(IV) sulfate ($Ce(SO_4)_2$) into dilute sulfuric acid (1/19 v/v). Two drops of indicator was added to a solution prepared by mixing 5 mL of sample and 10 mL diluted sulfuric acid (1/19 v/v). Then ceric sulfate solution was added dropwise to the sample solution until the color changed.

Due to the high solubility of CO_2 in water and the continuing changes in CO conversions with time on stream, it is difficult to obtain good carbon balance and assess the importance of the combustion pathway. This value, can however, be assessed by summing O_{xs} (defined as the O beyond what is required for stoichiometric CO oxidation) over the period of the experiment and comparing it with the total alkene reacted or epoxide formed. O_{xs} can be caluclated from R_{Oxs} which is the difference in the rates of oxygen **atom** and CO consumption (Eq. 2)

$$R_{Oxs} = 2^* R_{O2\ used} - R_{CO\ used} \quad (2)$$

The efficiency in O_{xs} production, E_{Oxs}, is defined as the ratio of O consumed for oxidation other than the production of CO_2 to CO consumed.

$$E_{Oxs} = R_{Oxs} / R_{CO} = \text{efficiency in } O_{xs} \text{ production} \quad (3)$$

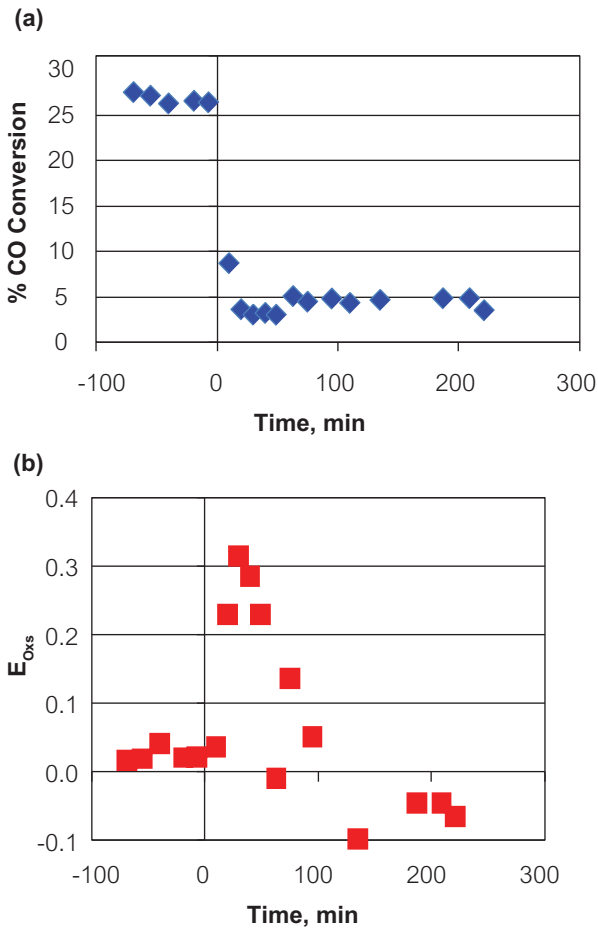
Results

3 a. Au/TiO_2

Figure 2a shows CO oxidation over a Au/TiO_2 catalyst at room temperature in a feed of 2.5% CO and 1.25% O_2 in He. Before t=0, the catalyst was suspended above the liquid and was relatively active for CO oxidation, albeit the activity was noticeably lower than when the same catalyst was placed in a plug flow reactor. At t=0, the catalyst was dispersed into the aqueous phase and the CO conversion decreased sharply due to the low solubility of the gases in H_2O. E_{Oxs} was zero in the gas phase but increased transiently to a value of ~0.3 before decaying to zero after around 100 min. When the experiment was repeated with half the amount of catalyst, the aqueous phase CO conversions and E_{Oxs} did not change significantly, suggesting that the rate limiting factor was not the amount of catalyst but the dissolution of gases. At the end of the experiment, with 0.05g Au/TiO_2 catalyst, there were 5.2 µmoles of H_2O_2 in the aqueous phase. This amount was less than the estimate of Oxs consumed, which could be due to handling loss and continual decomposition of H_2O_2 before titration. However the amount of H_2O_2 detected exceeded the amount expected from the equilibrium concentration of the oxidation of H_2O with O_2 by many orders of magnitude (K_{25}=.2.58*10^{-22} for H_2O oxidation with O_2).

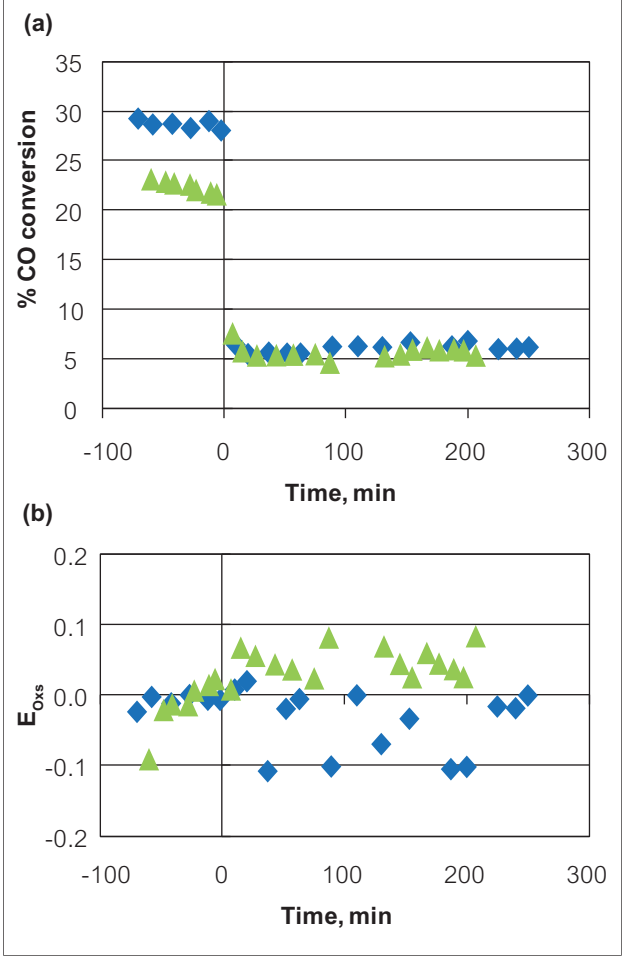
Figure 3a shows that when the H_2O temperature was increased to 40°C, CO conversions in the gas phase (gas phase temperature was less than 40°C) and aqueous phase increased slightly. When 1.25% 1-butene was included in the feed, CO conversion

Figure 2



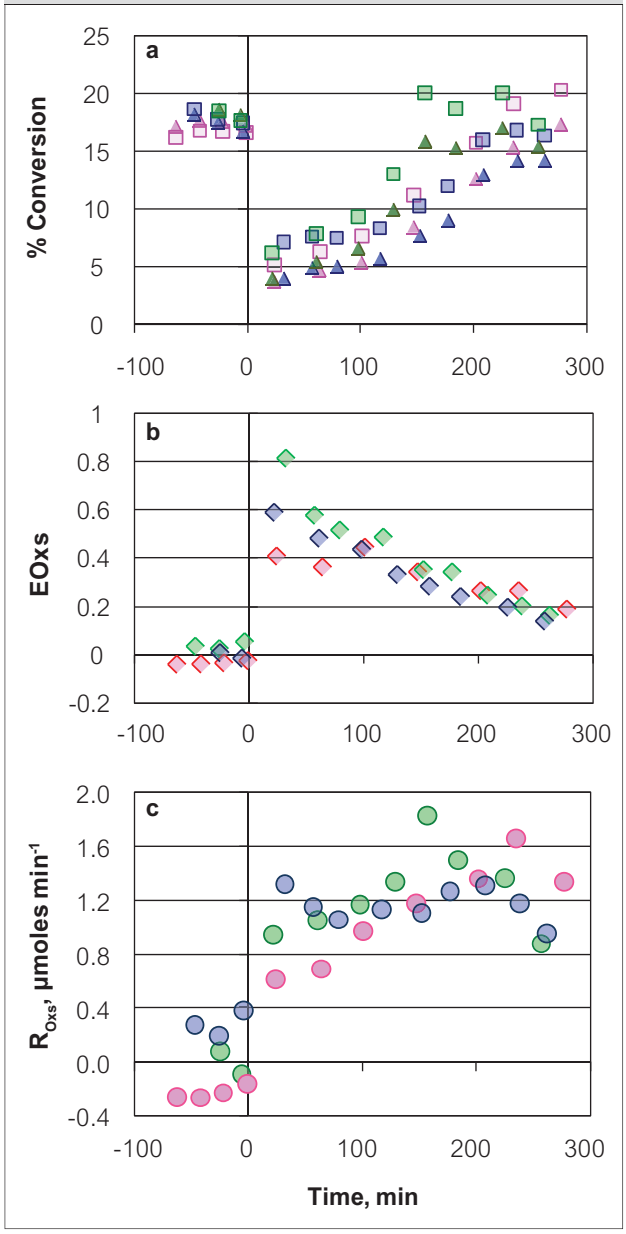
% CO conversion and efficiency in O_{xs} production (E_{Oxs}), as a function of time. Reaction condition: 2.5% CO, 1.25% O_2 and balance He, over Au/TiO_2 catalyst at 25°C

Figure 3



(a) % CO conversions and (b) E_{Oxs} over Au/TiO_2 catalyst at 40°C. ◊: feed contains 2.5% CO and 1.25% O_2 in He; Δ: feed contains 2.5% CO, 1.25% O_2 and 1.25% C_4H_8 in He

Figure 4



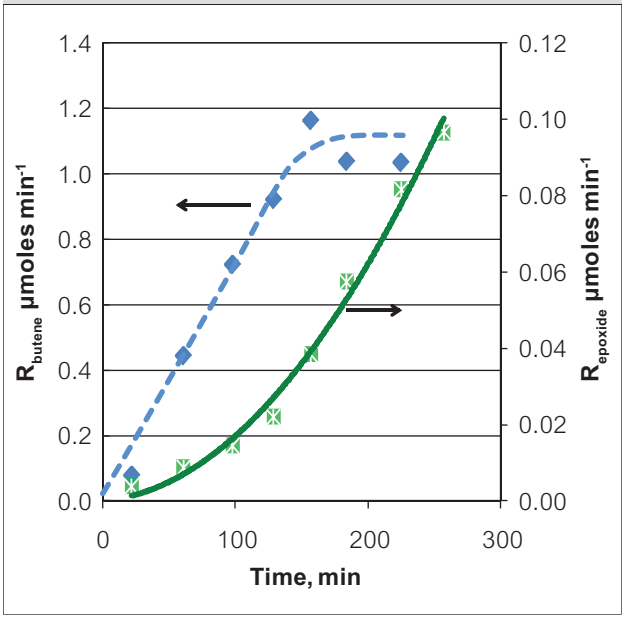
(a) % CO and O_2 conversions, (b) E_{Oxs} and (c) ROxs over Au/TiO_2+TS-1 binary catalytic system at 40°C. Feed composition: 2.5% CO, 1.25% O_2, 1.25% butene, balance He. □: O_2 conversion, Δ: CO conversion; ◊: E_{Oxs}, O: R_{Oxs}. Each color set for 4(a), (b) and (c) corresponds to the same run

was slightly suppressed in the gas phase but remained unaffected in the aqueous phase. The E_{Oxs} was close to zero, with and without butene in the feed, and was much less than that observed under room temperature reaction condition (Fig. 3b).

3b. Au/TiO_2 + TS-1 catalyst activity

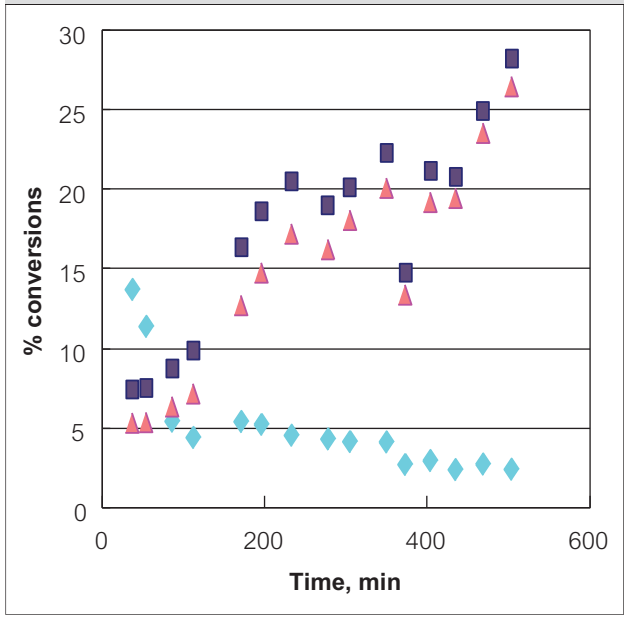
Figure 4a shows the CO and O_2 conversions for three separate runs in a feed of CO, O_2 and 1-butene using the binary catalyst system of Au/TiO_2 + TS-1. CO conversion in the gas phase was lower than the runs without TS-1 because diffusional effect was more severe in a deeper bed in the polyethylene cup due to the presence of TS-1. In the gas phase, within uncertainties, the O_2 and CO conversions were identical. Once the catalysts were dispersed into the aqueous phase, O_2 conversions were always higher than the corresponding CO conversions. Both CO and O_2 conversions increased with time on stream until at the end of the experiment their conversions were similar or higher than that of the initial gas phase conversions. However, there was no parallel increase in the rate of O_{xs} production (Fig. 4c).

Figure 5



Rates of butene consumption and butene 1,2-epoxide formation as observed in the gas phase. Reaction conditions same as Figure 4

Figure 6



Conversions as a function with time on stream over Au/TiO_2+TS-1 in the aqueous phase at 40°C. Feed composition same as Figure 4. □ O_2 , Δ CO, ◊1-butene.

Table 1: Products distribution in CO assisted 1-butene epoxidation in the aqueous phase at 40°C

Run #	Catalyst	Feed	Quantity, x10^{-5} moles				
			Total Epoxide (gas/liquid)	Diol	O_{xs}	Butene consumed	H_2O_2[b]
1	Au/TiO_2+TS-1	$CO+O_2+C_4H_8$	3.0 (0.8/2.2)	15	31	19	0.4
2	Au/TiO_2+TS-1	$CO+O_2+C_4H_8$	2.0 (0.6/1.4)	14	30	29	0.3
3	Au/TiO_2+TS-1	$CO+O_2+C_4H_8$	3.6 (0.7/2.9)	18	30	26	0.6
4	Au/TiO_2+TS-1	$O_2+C_4H_8$	0	0	0	0	0
5	Au/TiO_2+TS-1	$CO+O_2$	ND[a]	ND	~6	ND	ND
6	TS-1	$CO_2+O_2+C_4H_8$	0	0	0	0	0
7	Au/TiO_2+ silicalite	$CO_2+O_2+C_4H_8$	trace	0	0	not detectable	0.6

[a] ND= not determined
[b] The errors are large for these values, estimated ± 20% because of small concentrations, handling losses, and continual decomposition of H_2O_2 during set up for its titration

Upon dispersion of the catalysts into H_2O (t=0), butene 1,2- epoxide was detected in the gas phase. The epoxide amount detected in the gas phase was low initially, as most of it was dissolved in H_2O, but grew with time as the solution concentration increased (Fig. 5). Gas phase butene consumption was low initially as dissolved butene was utilized first ($5.62*10^{-5}$ moles was dissolved in 50 mL H_2O as calculated from ref 18) and the steady state was only reached after 150 min. Thus the total butene consumed was calculated using the steady state value of butene reacted, integrated over the duration of the experiment. The products formed and butene consumed in three separate reactions under identical feed conditions are tabulated as runs 1-3 of Table 1. The variability in the data may arise from the manner

the feed gas and catalysts were dispersed in the liquid. Runs 4-7 of Table 1 show that when one of the essential components of the reaction, CO, C_4H_8, Au/TiO_2, or TS-1 was omitted, O_{xs} was very low or absent and there was no oxygenated hydrocarbon product.

In a separate extended time experiment (Fig. 6), in which the catalysts were placed in H_2O right at the beginning (thus, the data before 80 min are not steady state data), it was observed that even after 500 min, CO and O_2 conversions appeared to be continually increasing while butene conversion appeared to be steady for a while before it declined with long time on stream. The increases in CO and O_2 conversions were only observed in the binary catalytic system of Au/TiO_2 and TS-1 and were not observed for Au/TiO_2 catalyst alone or Au/TiO_2 and silicalite, which has the same crystal structure as TS-1 but without Ti incorporation, or when butene was omitted from the feed.

Discussion

The possible role of peroxy in CO oxidation over supported Au catalyst has been suggested by DFT calculation [19, 20]. We have proposed [21] that this peroxy species may interact with H_2O to form H_2O_2 with the remaining O atom used in CO oxidation. Conversely, CO could interact with this peroxy first and the remaining O proceeds to react with H_2O to generate H_2O_2. We favor the first pathway because we think that the peroxy species is more reactive than the [O] atom deposited as a result of CO oxidation, and therefore more likely to oxidize H_2O. The resultant H_2O_2 could decompose (Eq. 4) or react with CO to form CO_2 (Eq. 5). As defined, R_{Oxs} is the rate of O consumption beyond what is required for stoichiometric CO oxidation, and is proposed to be the net rate of H_2O_2 generation:

$$H_2O_2 \rightarrow H_2O + 0.5O_2 \quad (4)$$

$$H_2O_2 + CO \rightarrow CO_2 + H_2O \; H_2O_2 \quad (5)$$

The highest E_{Oxs}, net H_2O_2 generated per mole of CO reacted, was 0.3 upon transfer of Au/TiO_2 into the aqueous phase at room temperature (Fig. 2b). This efficiency rapidly decreased as the solution H_2O_2 concentration built up and reactions (4) and (5) became significant. When E_{Oxs} reached zero, the formation rate of H_2O_2 was balanced by its decomposition/ reduction rates. That this decrease in E_{Oxs} was not related to any changes in the catalytic CO oxidation characteristic could be deduced from the fact that CO conversion remained constant with time (Fig. 3a). The reactions shown by Eq. 4 and / or Eq. 5 became more rapid at 40°C and E_{Oxs} was almost zero within uncertainties in a feed of $CO+O_2$, with or without butene.

On the other hand, when H_2O_2 was harnessed by reaction with 1-butene (Eq. 6) in the presence of TS-1, the non-productive reactions of H_2O_2 are deterred and the initial E_{Oxs} was very high (Fig. 4b); almost approaching unity. This E_{Oxs} also decreased with time on stream, but the change was mostly due to increase in CO conversion (Fig. 4a). In fact, within uncertainties, R_{Oxs} remained constant with time on stream (Fig. 4c).

$$H_2O_2 + R\text{-}C{=}C \rightarrow RC_2O + H_2O \quad (6)$$

Butene 1,2-epoxide was detected in the exit gas, formed by reaction of butene with H_2O_2 and also in the product solution (Eq. 6), when a mixture of Au/TiO_2 and TS-1 were used as the catalysts. Table 1 shows that in addition to epoxides, 1,2 butane diol was detected in the product solution as the major oxygenated hydrocarbon product. This suggests rapid hydrolysis of the epoxide in an aqueous medium. The sum of hydrogen peroxide, epoxide and diol was smaller than that of the total O_{xs}, albeit not by an amount that would suggest combustion of butene as a significant pathway as the total combustion of one mole of butene to CO_2 and H_2O would require 12 moles of O_{xs}. The fact that the alkene consumed integrated over time was close to O_{xs} is also consistent with the fact that combustion of alkene is not a major pathway. Table 1 also shows that the formation of epoxide/diol requires Au/TiO_2 (run #6) and CO (run #4). In fact, there were no reactions in those two runs. Isolated Ti site is also important because when TS-1 was replaced with silicalite (run #7) only trace amounts of epoxide were detected in the product solution although CO oxidation was detected.

The increase in CO and O_2 conversions with time (Fig. 4a and Fig. 6) implies the generation of a new catalytic species active for CO oxidation. The generation of this new species requires the presence of TS-1. It was not formed when the reaction solution contains only Au/TiO_2 or when TS-1 was substituted by silicalite (data not shown) in the catalytic system. It is catalytically distinct from Au/TiO_2 as CO oxidation does not result in the generation of O_{xs}. It is probably formed through

solubilization of Ti from TS-1 and/or Au from Au/TiO_2; a process that depletes the components essential for epoxide formation and thus accounts for the eventual drop in butene conversion for the extended time experiment (Fig. 6).

Conclusion

A Au/TiO_2 +TS-1 binary catalytic system catalyzes low temperature epoxidation of 1-butene in the aqueous phase. Butene 1,2-epoxide was formed but was extensively hydrolyzed to 1,2-butane diol. During the aqueous phase epoxidation reaction, a new species of highly reactive CO oxidation catalyst appears to be generated and there is evidence that the new catalyst is made up of both Au and Ti.

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